

STUDIES IN CONVERSION OF BUTYLENES TO BUTADINE

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in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

55807

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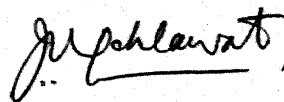
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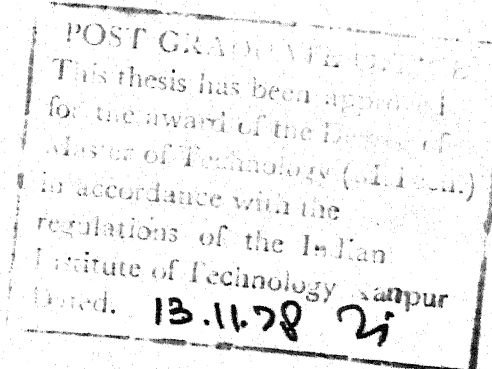
C E R T I F I C A T E

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DEFINITIONS-AND-NOTATIONSDEFINITIONS :

- 1 Conversion = $\frac{\text{moles of butylenes reacted per hour}}{\text{moles of butylenes fed to the reactor per hour}}$
- 2 Yield = $\frac{\text{moles of butylenes converted into butadiene per hour}}{\text{moles of butylenes fed to the reactor per hour}}$
- 3 Selectivity = $\frac{\text{moles of butylenes converted in to the butadiene per hour}}{\text{moles of butylenes reacted per hour}}$
- 4 Contact time = $\frac{\text{volume of catalyst}}{\text{volumetric feed rate}}$
- 5 Rate of reaction = $\frac{q - \text{moles of butylenes reacted}}{(\text{sec.}) (\text{cm}^3 \text{ of catalyst})}$

NOTATIONS :

- A, B, C, and D = constants
- r_A = rate of reaction
- K = reaction rate constant
- C_A = concentration of butylenes
- C_B = concentration of oxygen
- T = reaction temperature
- C_{AO} = initial concentration of butylenes
- C_{BO} = initial concentration of oxygen
- X_A = conversion
- ϵ_A = fractional ^{volume} change on complete conversion of butylenes .

SYNOPSIS

The production of butadiene from butylenes is industrially important. Butylenes may be obtained as by-product of petroleum processing, such as catalytic petro-cracking operations or from a non-petroleum source, such as ^{during} the production of butadiene from ethanol. Large quantities of butylenes are reported to be available as by-product from a synthetic rubber plant based on ethanol. In the present study butylenes were generated by the dehydration of sec-butanol using concentrated sulphuric acid as catalyst. The oxidative dehydrogenation process, with proper proportions of steam and air, was used for the conversion of butylenes to butadiene.

A fixed bed reactor of 38 mm diameter in stainless steel construction was used. The catalyst used, was in pellet form containing Fe_2O_3 (20.2%), MgO (3.7%) and Cr_2O_3 (2.4%) on Al_2O_3 (73.7%) as carrier. The surface area of the catalyst was $218 \text{ m}^2/\text{gm}$ and pore volume was 0.43 cc/gm .

A detailed study was carried out covering the reactor temperature range of 340 to 500°C . The oxygen to butylene ratio was varied from 0.33 to 0.8 and steam to butylene ratio between 1.8 to 5.2 .

The products of reaction were analysed by the gas chromatographic method. The maximum conversion of butylenes was found to be 26.2% at a temperature of 500°C with the

butadiene selectivity 94% and a yield of 24.6% .

The over all reaction was found to conform to first order kinetics with 0.5 order in butenes and 0.5 order in oxygen over a temperature range of 340 to 500°C . The apparent activation energy for the reaction was found to be 12.0 K-cal/gm-mole for the range of 340-400°C and 6.0 K-cal/g.mole for the temperature range of 400-500°C. The temperature conversion behavior of the reaction was also studied and the data were found to be correlated by the following cubical equation :

$$T = - 99.0 + 95.0 X - 6.3 X^2 + 0.136 X^3$$

The data obtained during this study are likely to be useful for an economic utilization of the butylene stream obtained as by-product from an indigenous synthetic rubber plant based on ethanol .

CHAPTER - I

INTRODUCTION

CHAPTER I

INTRODUCTION

Because of Japan's invasion of the rubber producing areas during the World War II the supplies of natural rubber were cut off to the rest of world. This led to an extensive research program for the development of synthetic rubber. Manufacture of butadiene, being a major constituent of synthetic rubber, gained importance. Different countries used different methods of manufacture of butadiene, depending upon the availability of raw materials. During World War II, the U.S. produced about 60% of its requirements of butadiene from ethyl alcohol but in 1945 the relative positions were reversed with about 60% of butadiene from petroleum¹. Later, the production of butadiene from alcohol in the United States was completely stopped in the favour of petroleum sources. Butadiene from petroleum continues to dominate the World scene. In India, however, butadiene is still manufactured from alcohol at Bareilly. The details of the process used at Bareilly plant have been described by Das². The main plant at Bareilly is the same as used in the United States for production of butadiene previously.

Routes to Butadiene Manufacture :

Butadiene may be manufactured by the following processes :

1. By dehydrogenation-dehydration of ethyl alcohol.
2. By steam cracking of hydrocarbons/naphtha.
3. By dehydrogenation of butanes.
4. By dehydrogenation of butylenes.

Various petroleum refining and processing operations produce large quantities of butylenes as byproduct. For example, during the steam cracking of naphtha for ethylene manufacture, a reasonable amount of butylenes is formed as a co-product. Similarly during the production of butadiene from ethanol, an appreciable amount of butylenes may be produced. Thus the butylenes (which may be available as a by product- either from petroleum cracking operations or during the conversion of ethanol to butadiene) may be found as an interesting feed stock for butadiene production.

The synthetic rubber plant at Bareilly produces butadiene from ethanol. This is the only one plant in the ^{commercially.} entire world today which manufactures butadiene from ethanol. About 800 tons of butylenes are produced per year as a by-product³. Presently this butylene stream is burnt as fuel. However, it may be more desirable and economical to convert this butylene stream into butadiene, which is

the main and desired product of the company. Hence the main object of this project was to conduct a process engineering study for the production of butadiene from butylenes which are available as a by-product from the synthetic rubber plant .

CHAPTER II

LITERATURE SURVEY

CHAPTER II

LITERATURE SURVEY

The proposal for the study of conversion of butylenes to butadiene is industrially important. A considerable amount of work has been done in this regard. The subject matter will be reviewed in the following sections:

2.1 Kinetics and Thermodynamics of Reaction :

The main reaction may be represented by the following scheme :



The reaction is highly endothermic, About 400 calories of heat is required per gram of butylene converted.⁴ It is a reversible reaction and a number of studies are available for finding equilibrium for the butylene dehydrogenation^{5,6} The work of Begley's⁶ is particularly significant for the prediction of the operating conditions of temperature and pressure for this reaction. His findings are summarized in tables 1 and 2 .

TABLE - 1

Butene Dehydrogenation Equilibria at Pressure-125 mm Hg and different temp.

Temperature °C	Moles per mole of input							
	250	365	480	590	700	760	820	870
1- Butene	0.0930	0.1279	0.1566	0.1470	0.0572	0.0301	0.0155	0.0077
Cis-2-Butene	0.2202	0.2136	0.2028	0.1488	0.0511	0.0252	0.0122	0.0057
Trans-2-Butene	0.3807	0.3380	0.3032	0.2155	0.0728	0.0353	0.0137	0.0078
1,2 Butadiene	0.	0.0001	0.0003	0.0016	0.0060	0.0092	0.0108	0.0135
1,3 Butadiene	0.1528	0.1612	0.2018	0.4503	0.7917	0.8633	0.8617	0.7416
1- Butyne	0.	0.	0.0001	0.0008	0.0034	0.0053	0.0073	0.0083
2- Butyne	0.0002	0.0003	0.0009	0.0037	0.0107	0.0144	0.0172	0.0176
Butadiyne	0.	0.	0.	0.	0.0002	0.0018	0.0147	0.0820
Vinylacetylene	0.	0.	0.	0.0001	0.0038	0.0148	0.0468	0.1157
Butane	0.1531	0.1589	0.1343	0.0381	0.0029	0.0007	0.0002	0.
H ₂	0.	0.0026	0.0688	0.4186	0.8171	0.9265	1.0346	1.2585

TABLE - 2

Butene Dehydrogenation Equilibria at Temperature 590°C and different pressure

Pressure	Moles per mole of Input				
	10 mm Hg	100 mm Hg	250 mm Hg	500 mm Hg	
1- Butene	0.0342	0.1320	0.1627	0.1749	0.1788 0.1826 0.1830 0.1832
Cis-2- Butane	0.0361	0.1393	0.1717	0.1846	0.1887 0.1929 0.1931 0.1933
Trans-2- Eutene	0.0523	0.2018	0.2487	0.2675	0.2734 0.2792 0.2798 0.2801
1,2 Butadiene	0.0030	0.0017	0.0012	0.0009	0.0008 0.0007 0.0006 0.0006
1,3 Butadiene	0.8621	0.4894	0.3460	0.2720	0.2411 0.1954 0.1853 0.1774
1-Butyne	0.0016	0.0009	0.0006	0.0005	0.0005 0.0004 0.0003 0.0003
2-Butyne	0.0071	0.0040	0.0029	0.0023	0.0020 0.0016 0.0015 0.0015
Butadiyne	0.0001	0.	0.	0.	0. 0. 0. 0.
Vinylacetylene	0.0022	0.0002	0.0001	0.	0. 0. 0. 0.
Butane	0.0012	0.0308	0.0681	0.0972	0.1146 0.1474 0.1562 0.1635
H ₂	0.8775	0.4657	0.2847	0.1786	0.1299 0.0507 0.0316 0.0163

It may be noted from the above that :

- 1) Butadiene yield increases as pressure decreases which is quite obvious and agrees with ~~Le-Chatelier~~ Principle.
- 2) Butadiene yield increases with temperature upto 760°C and decreases thereafter. For an endothermic reaction the yield increases with temperature, but at temperatures above 760°C , which is the cracking temperature, butadiene thus formed gets decomposed thereby resulting in reduction in its yield.

Limitation on Pressure and Temperature Range :

The above studies indicate that ~~at~~ the temperature and pressure of 760°C and 125 mm of Hg respectively, the butadiene yield is about 86%. It may also be noted that the same yield is obtainable at a temperature of 590°C and at a pressure of 10 mm Hg. It is known that butadiene would polymerise at high pressures and ultimately decompose to coke and hydrogen. This tendency can be minimised by operating at low hydrocarbon partial pressures. The work of Russel, Murphree and Asbury⁷ indicate that a pressure of 100 mm of Hg is the optimum to obtain higher catalytic selectivity and a reduced tendency of butadiene polymerization. This can be easily achieved by adding some inert gas as a diluent.

Further, it may be noted from the data given in Table - 1. that at temperatures below 450°C and a pressure of

125 mm Hg, the conversions are limited to about 30%. On the other hand to prevent thermal cracking of butylenes, it is necessary to avoid temperatures in excess of 760°C . Therefore the practical operating temperature range should be about $450\text{--}650^{\circ}\text{C}$ and the pressure about 100 mm of Hg.

2.2 Process Conditions and Evaluation:

Processes for the conversion of butylenes to butadiene may be classified as :

1. Thermal dehydrogenation of butylenes
2. Catalytic dehydrogenation of butylenes

It is reported that thermal dehydrogenation of butylene imposes the disadvantages of requiring more butylene raw material due to thermal cracking and consequent attainment of only about 40% of the theoretical yield of butadiene⁷ at 600°C and 100 mm Hg. Therefore, this process is to be considered unattractive. Accordingly emphasis has been placed on catalytic process to improve the yield of butadiene from butylenes.

Catalytic Dehydrogenation:

The principal processes for catalytic dehydrogenation may be classified as :

1. Houdry or conventional Dehydrogenation Process.
2. Steam Dilution Process.

3. Iodative Dehydrogenation process.
4. Oxidative Dehydrogenation process.

Houdry Dehydrogenation Process :

The Houdry dehydrogenation process^{8,9} is an adiabatic fixed bed process. The operating conditions are so chosen that the heat required for endothermic reaction is substantially equivalent to the exothermic heat of combustion of the coke deposited during the regeneration period. Differences between these heat quantities can be compensated for by the adjustment of the hydrocarbon feed or by temperature gain during regeneration for continuous operation. The catalyst employed is in the form of cylindrical pellets consisting of active alumina impregnated with chromic oxide. Catalyst is regenerated in the reactors by burning off the coke deposits with preheated air. Inert granular material of high heat capacity may be fixed with the active capacity of the catalyst bed .

The major process conditions are :

Temperature 550 - 650°C

Pressure 120- 150 mm Hg.

Steam Dilution Process :

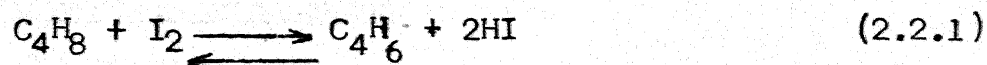
In this process the steam is used as a heat carrier, permitting adiabatic operation.^{10,11,12} At the same

time steam dilution reduced residence time, since a large volume of steam-butylene mixture goes through the reactor per unit time. Thus it takes care of two prime problems of heat supply and residence time. Also partial pressure of butylene is reduced by introducing steam and this helps to suppress side reactions, and remove some of the coke deposited on the catalyst.

The work of Stowe, Mayer and Cronerwett¹³ using "Dow Type-B" (calcium nickel phosphate) catalyst show that the conversion data are consistent with the kinetic model in which conversion rate is proportional to the number of active sites on the catalyst and to the fraction of the active sites covered by the butylenes. They used a temperature range of 550-675°C and obtained conversions of 50-72% with a selectivity of 85-99% .

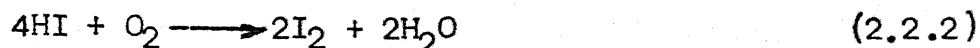
Halogenative Dehydrogenation Process :

Iodine has been found to be unique for the halogenative dehydrogenation process¹⁴. The overall reaction may be represented as follows :



It is a reversible reaction and requires a large excess of iodine. It refers mainly to a vapor phase process with no solid catalyst, in which air or oxygen is also introduced at various points into the reactor. The oxygen

apparently reacts with hydrogen iodide faster than with the hydrocarbon, thereby regenerating some of the iodine as per the following reaction.



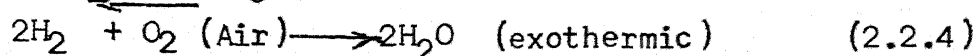
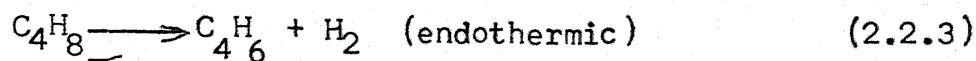
This internal regeneration of iodine in the reactor enables higher yields of butadiene to be obtained and reduces the ratio of iodine to hydrocarbon required to be fed to the reactor. Since reaction (2.2.2) is exothermic and reaction (2.2.1) endothermic, the use of oxygen also enables the reactor to be operated adiabatically without having to supply or remove heat through the reactor walls. A conversion of 76% has been claimed. But commercially this process is rather unattractive due to higher costs of iodine replacement and corrosive conditions.

Another route includes the chlorination of butenes and thermal dehydrogenation of chloro butenes¹⁵. However, it is found to be more expensive than selective dehydrogenation.

Oxidative Dehydrogenation:

In this process a mixture of steam, air and n-butylenes is passed over a fixed catalyst bed at a temperature of 475-600°C, in the reactor.¹⁶ It is claimed that as butylenes are dehydrogenated, the hydrogen so produced reacts

with the oxygen of the air to form water. The overall reaction may be represented as follows :



By removing hydrogen from the reaction environment, the dehydrogenation reaction would proceed to a greater extent than in ordinary dehydrogenation. A simultaneous feed of steam and air to the reactor, makes it possible for continuous regeneration of catalyst. The steam further serves as a means of controlling reactor temperature by acting as a heat sink, as it ~~absorbs~~ the heat released by a small amount of hydrocarbon oxidation. Further, as a diluent, steam has a beneficial effect on butylene selectivity to butadiene. It is reported that a butylene conversion of 61.6- 89.6% can be achieved with butadiene selectivity of 92.7- 97.7% .

A kinetic model for the oxidative dehydrogenation of butylene to butadiene over a ferrite catalyst has been produced by Sterrett¹⁷. They used a plug flow reactor in which reaction temperature was varied from 325- 375°C, butylene mole fraction was varied from 0.5 to 0.1 and oxygen mole fraction from 0.031 to 0.062 . Total pressure was one atmosphere, The formation of butadiene, did not follow any simple order kinetics, Aliev, Abilov and Aliev¹⁸

developed a mathematical model for fluidized catalyst beds. Their experimental data showed that reaction occurred in the kinetic region where the diffusion effect was negligible. The studies of Venyamimov, Sazonova and Alferova¹⁹ indicate that the yield of 1,3 butadiene can be increased by proper use of catalysts which possess isomerizing activity and control subsequent oxidation of 1,3 butadiene.

From the above review the oxidative dehydrogenation process for the conversion of butylenes to butadiene appears to be a better choice.

2.3 Catalyst for the Reaction :

A number of catalysts have been used for different processes. Since oxidative dehydrogenation process appears to be more attractive, the following discussion will be restricted to the catalysts used for this process in detail and for others in brief. Table 3 gives an idea about the various catalysts used for different processes :

TABLE - 3

List of catalysts for different processes

Process	Catalysts generally used	Activity Parameters	
		conversion	Selectivity
1. Conventional Dehydrogenation	Chromia- Alumina	23.4%	34.7%

2. Steam Dilution method	i) "1707" ⁷ (Fe ₂ O ₃ with K ₂ O, CuO and MgO)	20-40%	70%
	ii) "Shell-205" ¹¹	26-28%	73-75%
	iii) "Dow Type-B" ¹¹ (calcium nickel phosphate promoted with 20% chromium sesquioxide)	45-55%	90%
3. Iodative Dehydrogenation	Oxide and hydroxide of Ni and Li ¹⁴	50%	-
4. Oxidative Dehydrogenation	i) Ferrite	52%	93%
	ii) Cl ₂ or Br ₂ promoted ferrite	59%	95%
	iii) Magnesium ferrite	79%	95%
	iv) Magnesium chromium ferrite	69%	91%
	v) Metal Vanadate	62%	-
	vi) Bi ₂ O ₃ - 2(MoO ₃)	61%	90%

Catalysts For Non-Oxidative Dehydrogenation :

A study of dehydrogenation of butylene over a chromia alumina catalyst was done by Dodd and Watson.²⁰

According to them, the rate of dehydrogenation was found to be controlled by a surface reaction involving dual^{active} centres.

The overall selectivity of the reaction was reduced by the cracking of butylenes.

For steam dehydrogenation a number of catalysts have been described in the literature other than those given in table.³ Czarny and Worjick²¹ prepared a catalyst from calcium-nickel phosphate promoted with chromium phosphate. At 20 fold dilution with steam and at 640°C, this catalyst with 95% C₄H₈ gave 48% yield with 90% selectivity at atmospheric pressure. Another attempt made for increasing the selectivity, shows that increasing porosity of catalyst increased selectivity. For this purpose a catalyst was manufactured by making a paste of Fe₂O₃, powdered Cr₂O₃ and K₂CO₃ with water and dried at 110°C. The catalyst had a porosity of 50% and gave a selectivity of 80%.

Some other catalysts used for this purpose have been described by Green²² (comprising a major proportion of magnesium oxide and minor proportions of iron oxide, copper oxide and potassium oxide) and by Dow Chemical Co.²³ (Cr -oxide containing Ca-Ni phosphate catalyst and oxidant comprising Mg, Mn, Co, Ni, Zn or Cd ferrite modified with B and mixed with Fe₂O₃ catalyst).

Catalysts For Oxidative Dehydrogenation:

Most of the catalysts described for oxidative dehydrogenation of butylenes to butadiene are very active and selective, but their preparation is rather complex and expensive. But before describing the method of preparation

of a catalyst, it is desirable to summarize the various studies, to prepare a more active and selective catalyst.

- i) The activity of metal oxides on Al_2O_3 in the oxidative dehydrogenation of n-butylenes was studied at 300-600°C using a molar ratio of butylene:oxygen:steam of 1:1.5:20 using catalysts containing 10-15% of metal oxide having a specific surface area of 5-14 m^2/g . The activity for butadiene formation decreased in the following order :

$\text{Fe} > \text{Co} > \text{Mn} > \text{Mo} > \text{Ni} > \text{Sn} > \text{W} > \text{Pb} > \text{Bi} > \text{Cd} > \text{Zn} > \text{Mg}$

and the by-product formation increases in the order :

$\text{Mn} < \text{Cr} < \text{Cu} < \text{Co} < \text{Fe} < \text{Ni} < \text{Bi} < \text{Mo} < \text{Sn} < \text{Cd} < \text{W} < \text{Pb} < \text{Zn} < \text{Mg}$

The catalytic activity can be correlated with the energy of the metal-O-bond.

- ii) The activity and selectivity of Fe-Bi-Mo oxide catalysts in the oxidative dehydrogenation were higher than those of Bi-Mo catalysts. Catalysts with 2:1:1, Fe-Bi-Mo ratio or those on a support with 7:2:1-6:3:1 ratios had the best activity in the oxidative dehydrogenation of butylenes to the butadiene, which was obtained at 25-30°C lower than those using Bi-Mo catalysts. The most active catalysts were obtained by adding Fe into the Bi-Mo catalyst.

- iii) The rate of oxidative dehydrogenation of butylenes to butadiene was independent of the Fe_2O_3 concentration in the antimony-ironoxide catalyst below 42% Fe_2O_3 , but increased with the Fe_2O_3 concentration above 42%. The selectivity of the catalyst for the formation of butadiene was highest in the presence of iron antimonate.
- iv) The more gelatinous metal oxide precipitated in presence of polyhydric alcohol yielded a more active oxidative dehydrogenation catalyst. Miklas²⁴ claimed that a catalyst containing ferric and magnesium chloride with 2% glycerol yielded 74% butadiene from a butylene-oxygen steam feed at a bed temperature of 500°C.

2.4 Analysis and Recovery of Product Stream :

The usual methods used for butadiene analysis are :

- I. Gas Chromatography
- II. Chemical Analysis

2.4.1 Gas Chromatography :

Beckham and Libers²⁵ have given a gas chromatographic method for analyzing C_{1-5} hydrocarbons. According to them, n-dodecane and 1-dodecene exhibited superior resolving power for a C_{1-5} hydrocarbon blend. A 1:1 n-dodecane-1-dodecene mixture was used on a 0.25 cm.

inner diameter tubular column with flame ionization detector and helium as carrier gas .

AleKseeva and others²⁶ have also proposed gas chromatographic method for the determination of the components of the oxidative dehydrogenation of olefins and compounds containing oxygen. Two columns were used. The first for determination of O, N, CH₄ and C oxides, the other containing a diatomite support coated with polyethylene glycol ether for the separation of CO₂ and C₂₋₄ hydrocarbons. Hydrogen gas was used as the carrier gas. The methods of Madison²⁷ and Cvejnovich²⁸ are similar and are applicable to C₁₋₄ hydrocarbons analysis. Here three columns are needed: squalane on chromosorb followed by adiponitrile on chromosorb for hydrocarbon analysis and a molecular sieve for determination of inorganic gases.

Sramek²⁹ also used three columns DMS (Di methyl sulpholane) on chromosorb and polyethylene glycol on celite for CO₂ and hydrocarbons and a molecular sieve column for inorganic gases. The temperature of detector was kept at 30°C and helium was used as carrier gas at column temperature of 25°C.

2.4.2 Chemical Analysis :

Molten maleic anhydride at about 100°C is found to be a suitable reactant for the quantitative determination

of butadiene in complex gas mixtures. Studies of Hans Tropsch and Mattox³⁰ indicate that other olefins do not react with maleic anhydride and have no influence on the butadiene determination, which is selectively absorbed and reacted with maleic anhydride at 100°C. However the gaseous hydrocarbons have appreciable physical solubility in the molten anhydride, and in order to reduce this physical solubility to the minimum, small amounts of the anhydride must be used. A special absorption pipette with which gas absorption could be made with less than 2 ml of adsorbent was used.

2.4.3 Recovery of Butadiene:

For recovery of butadiene from the product stream either ammoniacal cuprous salt solution³¹ or NMP (N-methyl pyrrolidone)^{32,33,34} can be used as a solvent for its extraction from the gaseous stream.

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CHAPTER - III

PROPOSED PROGRAM OF - WORK

CHAPTER - III
PROPOSED-PROGRAM-OF-WORK

3.1 Process Evaluation:

As discussed elsewhere for the conventional dehydrogenation process, with chromia-alumina as catalyst at atmospheric pressure, the selectivity is generally less than 50%. The selectivity may be increased to about 80% by operating at a pressure of 100 mm of Hg .

In order to avoid the problem of butadiene polymerisation and of low selectivity at higher pressures, it would be advantageous to use a heat carrying diluent such as steam, as in steam dilution process, with feed butylenes. This would provide sufficient heat capacity to reduce the temperature drop through the catalyst bed and simultaneously lower the butylene partial pressure to the desired range of 100 mm of Hg. Another important advantage using steam as diluent, is that the steam would react with coke on the catalyst to form the water gas at the temperature employed for the dehydrogenation of butylenes, along with the prevention of coke formation, occurring on catalyst surface, which reduces the activity of catalyst during reaction time. Also the formation of water gas with the coke and steam is an exothermic reaction providing, thereby, heat for the dehydrogenation reaction which is endothermic.

Unfortunately the steam dilution process with all its inherent advantages, gives only ^aconversion of 35.5% with selectivity of 75% at a temperature of about 500°C.

The difficulty of lower conversions in steam dilution process made halogenative dehydrogenation more attractive. This appeared capable of yielding a dehydrogenated C₄ product containing approximately 50% weight of butadiene and also requires approximately 1.5 tons of C₄ feed stock per ton of butadiene produced as compared to 1.8 tons required for Houdry process. But it is questionable the savings so obtained would be sufficient to offset the iodine losses and the cost of the iodine recovery system, since this process requires about 2 tons of iodine per ton of butadiene produced. Iodine being costlier than butadiene, the problem of iodine recovery is much important. A further problem inherent in this process is the possible formation of organo-iodine compounds by the reaction between butadiene and iodine. On the other hand oxidative dehydrogenation process, gives a very high yield of butadiene, using iron oxide as catalyst. Also when butadiene conversion is in the range of 75-80% the selectivity of butadiene is reasonably high at 88-92%. The reason of this tremendous increase in yield is that hydrogen released in dehydrogenation reaction, reacts with the oxygen of air, removing the

hydrogen from reaction environment and permitting the dehydrogenation reaction to go to a greater extent.

Thus, the oxidative dehydrogenation is commercially more attractive than the rest of the processes. In later chapters an attempt has been made to make a systematic study of the oxidative dehydrogenation of butylenes to butadiene.

3.2 Catalyst Selection Criteria :

The literature studies of section 2.3 indicate that iron oxide should be the major constituent of the catalyst since iron gives the best yield of butadiene. Further the addition of the oxide of Co would simultaneously reduce the possibilities of byproduct formation and undesirable side reaction. Further, the presence of 0.1-4 wt % polyhydric alcohol such as glycerol in the catalyst would yield a more gelatinous metal oxide, having sufficient mechanical strength and thermal stability. Thus a catalyst may be prepared by mixing oxides of Fe, Co, Mn and Cr in appropriate proportions with some amount of glycerol and halogen to improve its activity as well as yield. The surface area of such a catalyst should be of the order of $200 \text{ m}^2/\text{g}$. It is expected that a catalyst of the above proposed composition would produce better results .

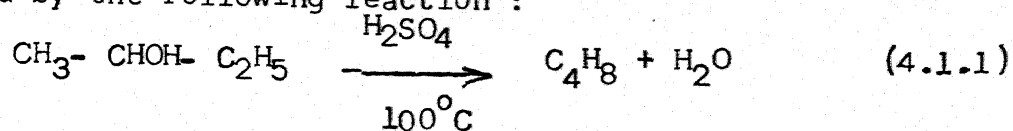
CHAPTER - IV

EXPERIMENTAL WORK

CHAPTER - IV
EXPERIMENTAL WORK

4.1 Generation of Butylenes:

Butylenes were generated by the dehydration of secondary butanol, in the presence of concentrated sulphuric acid at 100°C. A mixture of butene-1 and butene-2 is formed by the following reaction :



The apparatus used for the generation of butylenes is given in fig. 1. A conical flask containing mixture of concentrated sulphuric acid and sec-butanol was placed in a heating mantle. The temperature of the heating mantle was controlled by using a variable transformer (variac). The gas thus generated was collected in an assembly of aspirator bottles by water displacement method.

The butylene contents in the gas stream was determined by the gas-chromatographic analysis. The purity of the stream was found to be 99%. The composition of the butylenes generated as above is given in table- 4.

- A - Heating mantle
- B - Condenser
- C - Separating funnel
- D - Aspirator bottle assembly

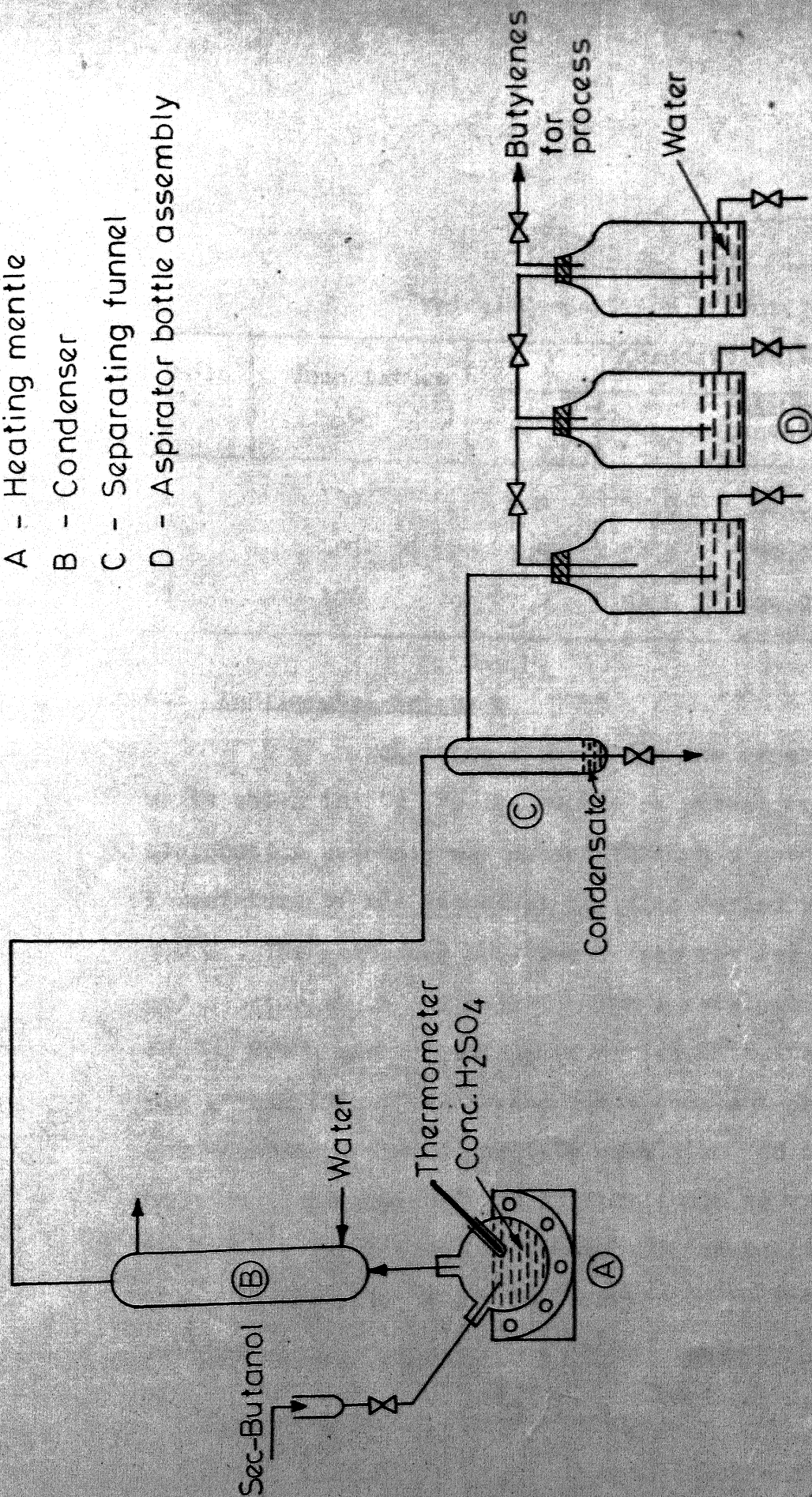


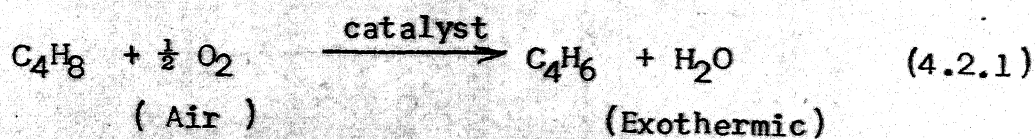
Fig. 1 : Schematic diagram for butylene generation.

TABLE - 4
Typical Composition of Butylenes

Sample No.	Temperature °C	Composition(%)			
		Butene -1	Trans-Butene -2	Cis-But-ene-2	Others
1	90	5.0	59.0	36.0	-
2	95	5.5	54.5	39.8	0.2
3	100	7.2	53.6	39.2	-

4.2 Experimental Set up :

A schematic diagram for the experimental set up is shown in fig. 2. The butylenes stream from the aspirator bottle assembly was passed through a preheater. The temperature of the preheater could be varied from 210°C to 600°C . The preheated butylene stream was fed to the fixed bed reactor which was filled with a catalyst containing Fe₂O₃, Cr₂O₃ and MgO on Al₂O₃ carrier. Simultaneously an air stream from a compressor (at a constant pressure of 5 psig) and steam generated separately were also fed to the reactor. The temperature of the reactor could be varied from 200°C to 900°C . The oxidative dehydrogenation reaction that takes place in the reactor may be represented by the following reaction :



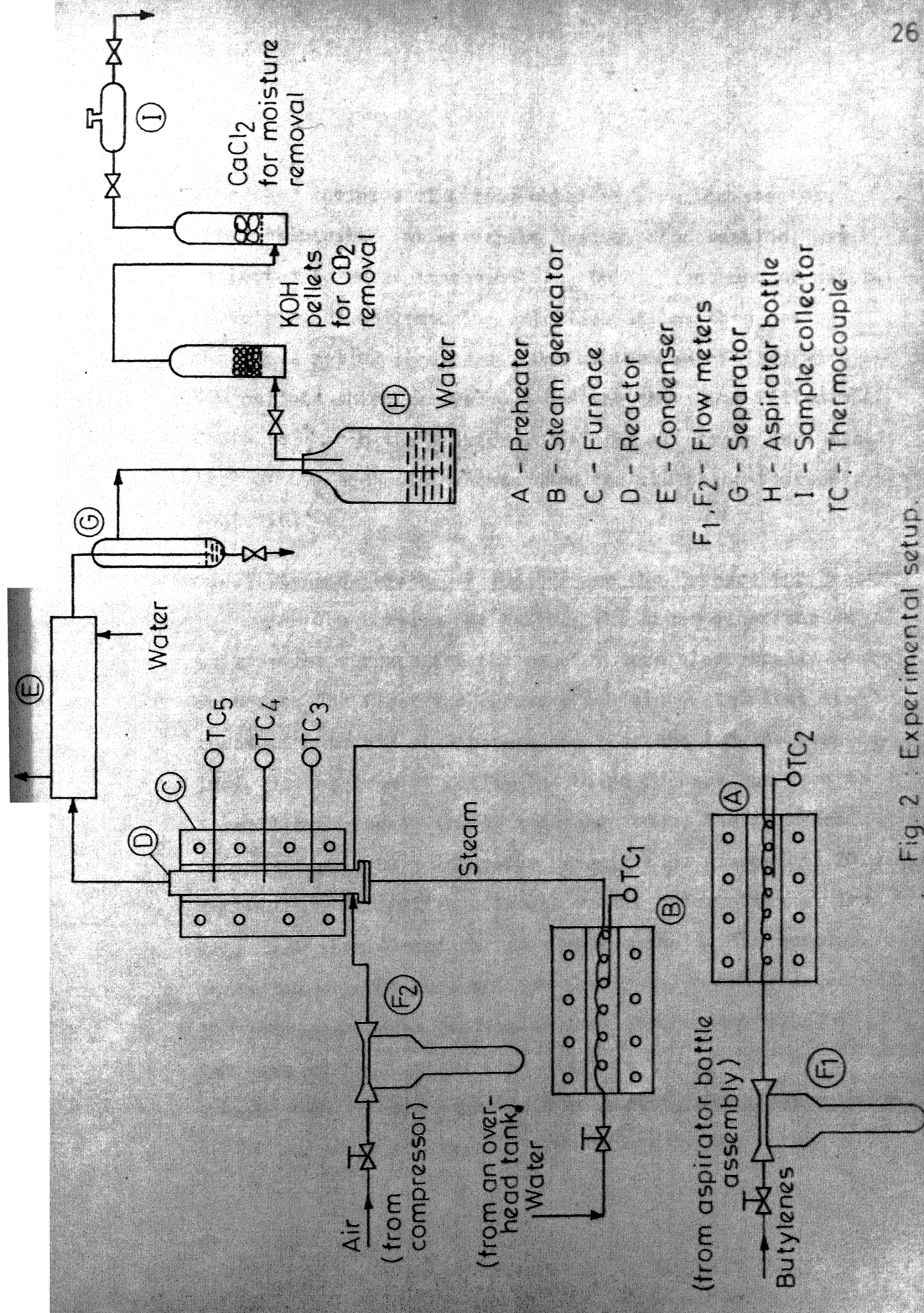


Fig. 2 : Experimental setup.

The product stream obtained from the reactor, after eliminating water vapors through condensation, was collected in an aspirator bottle, by displacement of water, containing dissolved sodium chloride. It was then passed through a set of absorbers. One of them was filled with KOH pellets which removed CO_2 and the other was filled with CaCl_2 to absorb the moisture. The product stream essentially free of CO_2 and moisture was used for the chromatographic analysis.

4.2.1 Steam generator, Preheater and the Furnace for Reactor:

The butylene preheater, the steam generator as well as the furnace for the reactor were electrically heated furnaces. The first two furnaces contained stainless steel tubes of 6 mm dia of 3 meters and 5 meters lengths respectively in the form of coils. The third furnace was used to install the reactor inside a ceramic tube. The furnaces consisted of a 50 mm diameter ceramic tube wrapped in 20 gauge kanthal wire of suitable length on the outer surface. The tube was then placed in an aluminium shell. The annular space between the tube and the shell was densely packed with the magnesia powder used as an insulating material. The two ends of the kanthal wire windings were joined to a standard 15 ampere porcelain connector, which was connected to the power source. The temperature of the furnaces

were regulated by the use of variable transformers (variacs) A temperature of 900°C could be easily attained in the furnace.

4.2.2 Capillary Flow Meters:

Two capillary flow meters, F_1 and F_2 , made of glass were installed in the apparatus, with U-tube manometers. They were used to record the flow rates of butylenes and air. The flow meters were made of 1 mm diameter and 70 mm long capillary tubes and water was used as manometric fluid. Calibration of flow meters were done by using soap bubble flow meter at room temperature (30°C). The calibration charts are given in fig. 3 and 4.

4.2.3 Reactor :

The details of the reactor are shown in fig. 5. It was made of a 50 cm long 38 mm diameter stainless steel tube. The lower end of the reactor was flanged and was bolted to a plate having a 6 mm size stainless steel tube in the centre used as the inlet for steam. The inlets for butylenes and air were provided near the bottom of the reactor and were made by welding 6 mm diameter stainless steel tubes at the outer periphery of the reactor. A 6 mm diameter stainless steel tube welded to the top of the reactor was used as outlet for the product stream. Three thermocouple protection tubes were fixed on one side of the reactor

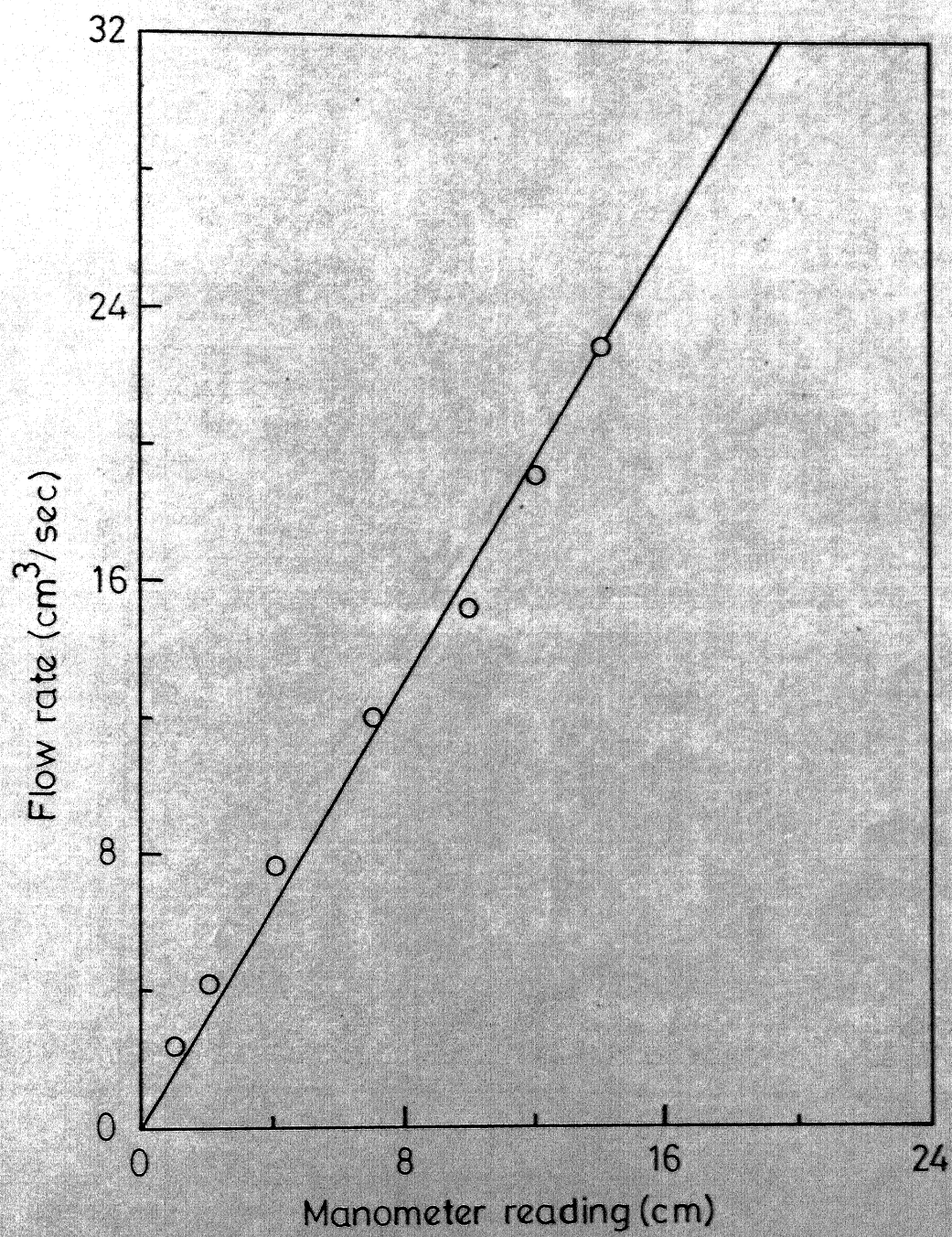


Fig. 3 : Calibration chart for capillary flowmeter for air.

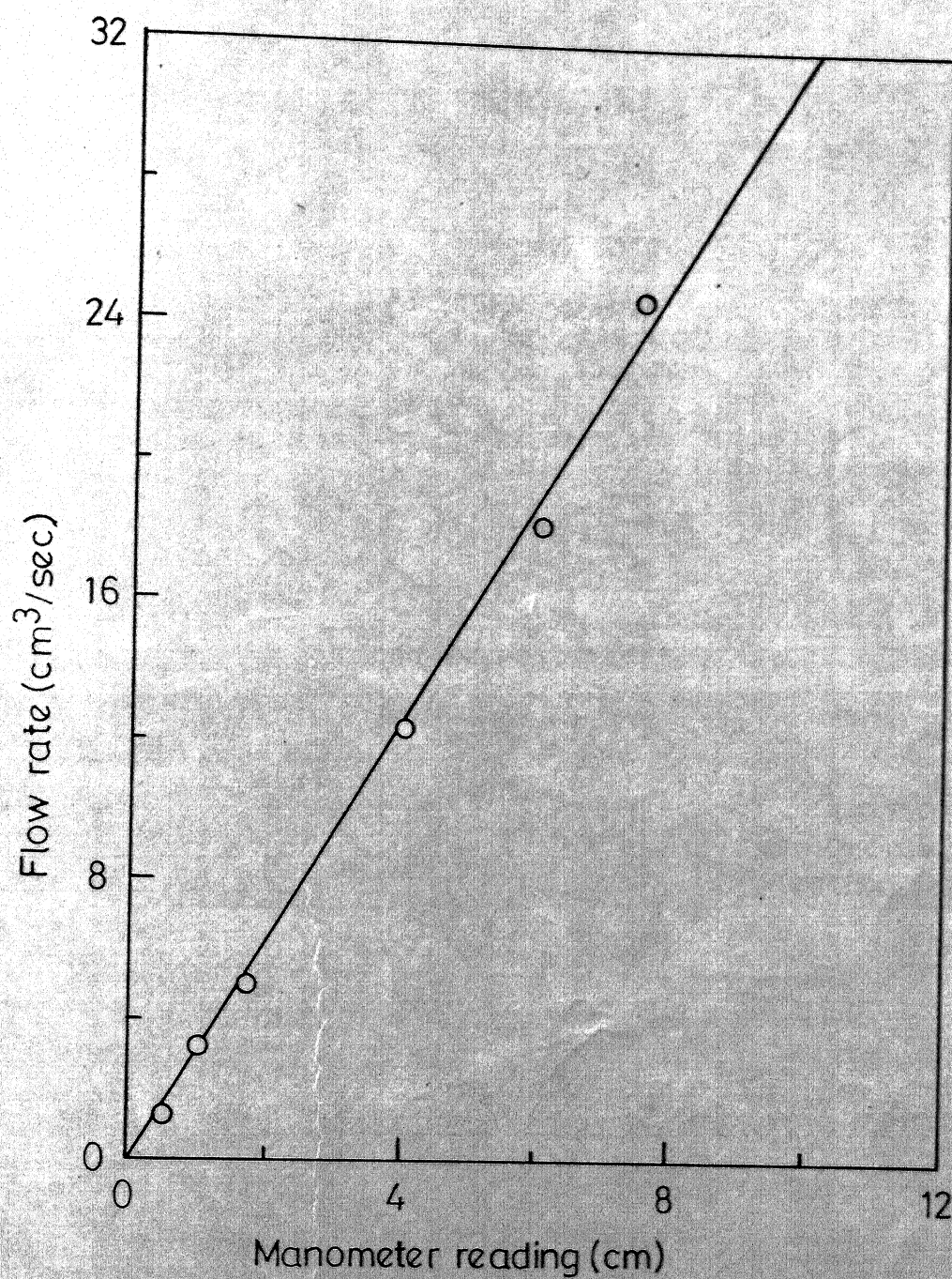


Fig. 4 : Calibration chart for capillary flowmeter for butylene.

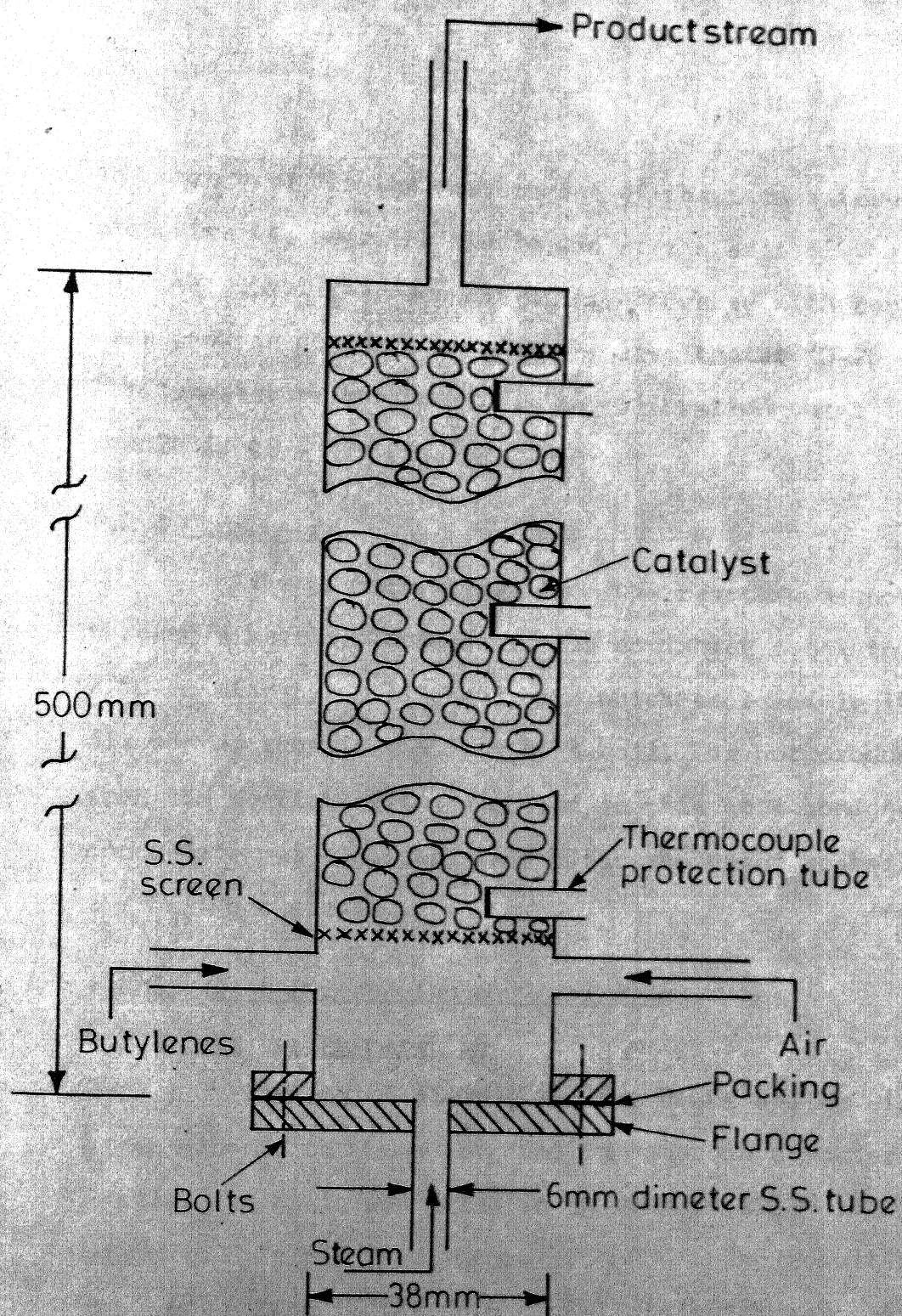


Fig. 5 : Reactor details.

and were used for the measurement of the temperature at the entrance, near the middle and at the exit of the reactor. Chromel Alumel thermocouple wires, (covered with ceramic beads) were used in conjunction with a milivoltmeter (0-25 mV), for temperature measurement. The calibration curve for thermocouple is given in fig. 6 .

4.2.4 Condenser:

The product stream from the reactor was passed through a metallic condenser. The condenser consisted of a 50 mm diameter mild steel pipe which enclosed in it a 3 mm dia copper tube in the form of a coil. The hot product stream from the reactor exit was cooled in this coil condenser. The condensate was collected in a glass separator installed in the exit gas stream .

4.3 Catalyst Preparation and Activation :

4.3.1 Catalyst Preparation :

A paste of Al_2O_3 , Fe_2O_3 , Cr_2O_3 and MgO in the given proportion was prepared in water in a mortar with pestle. The paste was dried in an oven at 120°C for 12 hrs and then calcined for 2 hours at 450°C . The resulting powder was pressed in the form of pellets which were again calcined at 600°C for 10 hours to obtain better dimensional stability. The catalyst prepared as above was characterized

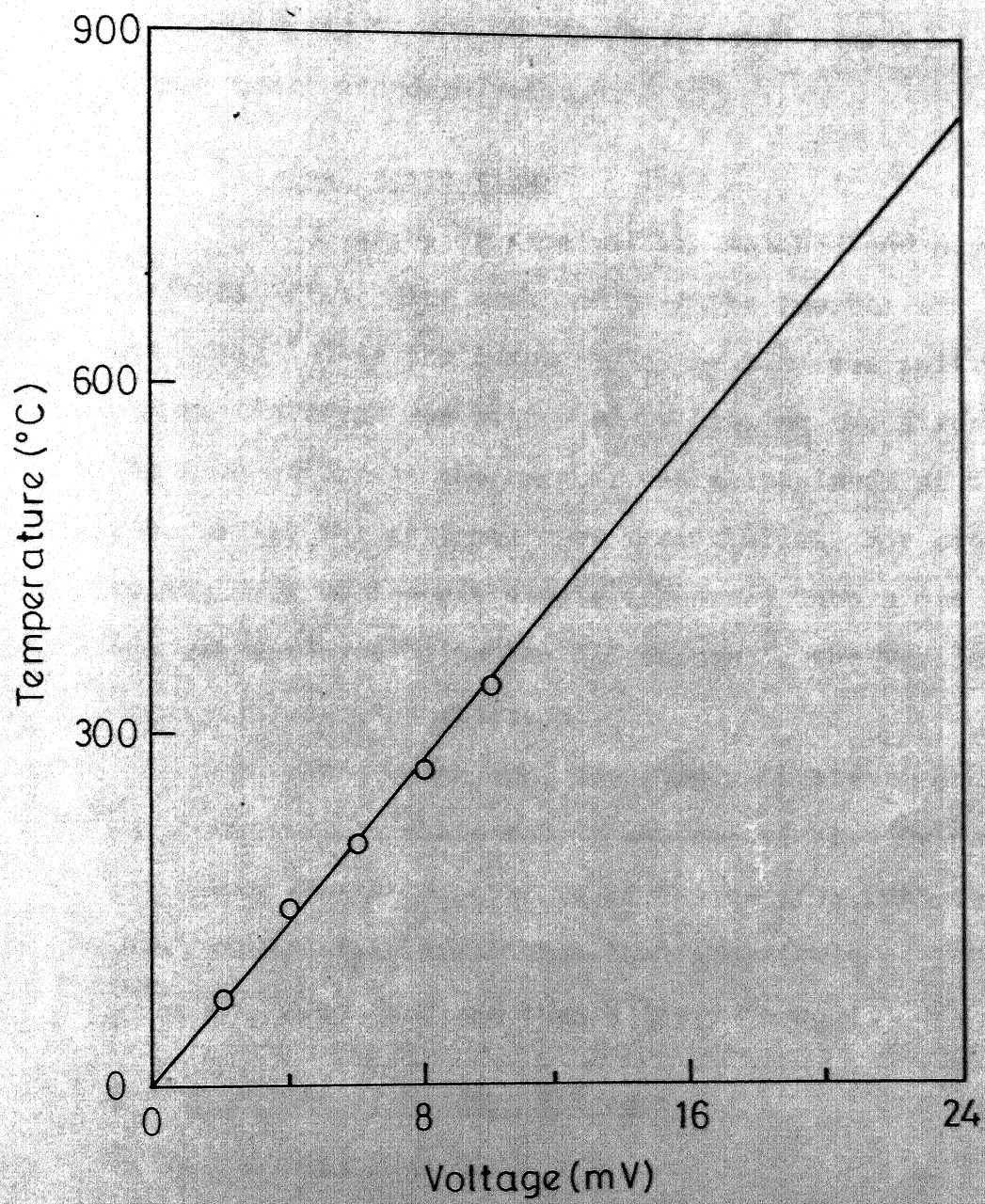


Fig. 6 : Calibration curve for thermocouple.

at the R&D department of M/s. Associated Cement Co. Ltd., Bombay using standard methods.

4.3.2 Catalyst Activation:

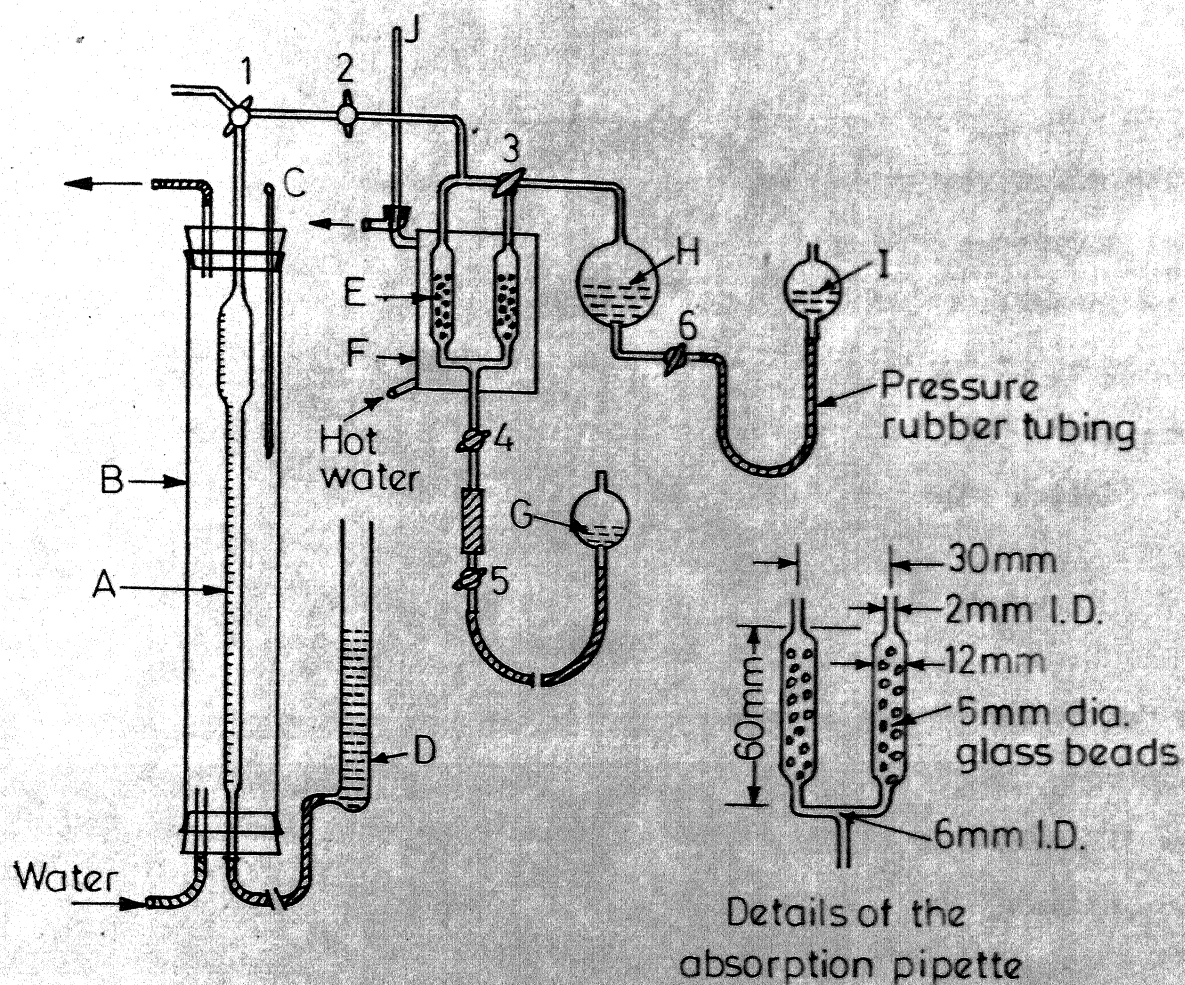
35 grams of catalyst was weighed and placed over the stainless steel wire mesh and then the reactor was assembled and installed in the furnace. The heating was switched on and the catalyst was activated by passing the stream of air. The temperature of the reactor was maintained at 650°C , for 2 hours for the activation of the catalyst. For product analysis, 5 ml of the gas sample was drawn into a gas syringe and was analysed using the DMS column in the Perkin Elmer Model 820 gas chromatograph.

After each run, the supply of steam and butylene were cut off and the catalyst was reactivated by passing the air alone at the temperature of the reactor furnace for about 30 minutes. After that the temperature of furnace was gradually decreased and then allowed to cool.

4.4 Analysis of Product Stream :

4.4.1 Chemical Analysis :

The molten maleic anhydride reacts with butadiene selectivity and can be conveniently used for its determination from a gas stream. The absorption pipette shown in fig. 7. was used for its determination. It was similar to the absorption pipette used by Gehlawat.^{35,36} About 100 ml of the gas



- A - Gas burette
- B - Cold water jacket
- C, J - Thermometers
- D - Levelling tube containing mercury
- E - Absorption pipette
- F - Jacket for hot solution
- G, H, I - Bulbs containing mercury
- 1-6 - Stopcocks

Fig. 7 : Apparatus for butadiene analysis by reaction with Molten Maleic Anhydride.

from the product stream was taken for a few preliminary runs and the gas was absorbed in molten maleic anhydride (A.R.) at 90°C. However, these results were not consistent with the results obtained by the gas chromatographic method at lower concentrations of butadiene. Later, because of the cumbersome procedure this method was dropped in favor of the more reliable and faster gas chromatographic method.

4.4.2 Gas Chromatographic Analysis:

A Perkin Elmer Model 820 gas chromatograph was used for gas analysis. The DMS column used for product analysis was made of a 6 mm diameter aluminium tube. It was borrowed from M/s. Synthetics and Chemicals Limited, Bareilly. The details of the column are given below :

Column material	DMS-E (Dimethyl-sulpholane)
Support material	G-C- 222
Length of column	7.75 meters
Particle size	60- 80 mesh
packing density	0.62317 gms/ml volume .

CHAPTER - V

RESULTS- AND- DISCUSSIONS

CHAPTER - V

RESULTS- AND- DISCUSSIONS

5.1 Catalyst Characteristics:

The catalyst used in this study was characterized at the R&D department of M/s. Associated Cement Companies Ltd., Bombay.³⁷ The chemical analysis and the physical properties of the catalyst are given in tables 5 and 6 .

TABLE - 5

Chemical Analysis of Catalyst

Sl.No.	Component	% by weight
1	Al_2O_3	73.2
2	Fe_2O_3	20.2
3	Cr_2O_3	2.4
4	MgO	3.7

TABLE- 6

Physical Properties of Catalyst

Sl.No.	Property	Data
1	Bulk density	0.705 gm/cm^3
2	Surface area	$218 \text{ m}^2/\text{gm.}$
3	Pore volume	0.43 cc/gm.

5.2 Preliminary Runs :

The preliminary test runs were carried out by varying the reactor temperature in the range of 200-900°C and the preheater temperature in the range of 240-600°C. The butylenes to oxygen ratio was varied from 0.02 to 1.0 (volume basis). Samples were collected in the glass collector equipped with a septum. The gas samples were analysed chromatographically. Helium at a flow rate of 50 ml/min. was used as the carrier gas. The temperatures of the column oven and the thermal conductivity detector were maintained at 35°C and 40°C respectively. A typical chromatogram is shown in figure 8. The retention times for different components at these conditions are given in table 7.

TABLE - 7

Retention Times of Different Components in G.L.C. Analysis

Sl.No.	Components	Retention times (Minutes)
1	Oxygen	4.0
2	Ethylene	5.3
3	Propylene	6.9
4	Butene- 1	16.2
5	Trans-Butene-2	19.7
6	Cis-Butene-2	22.4
7	1,3 Butadiene	31.1

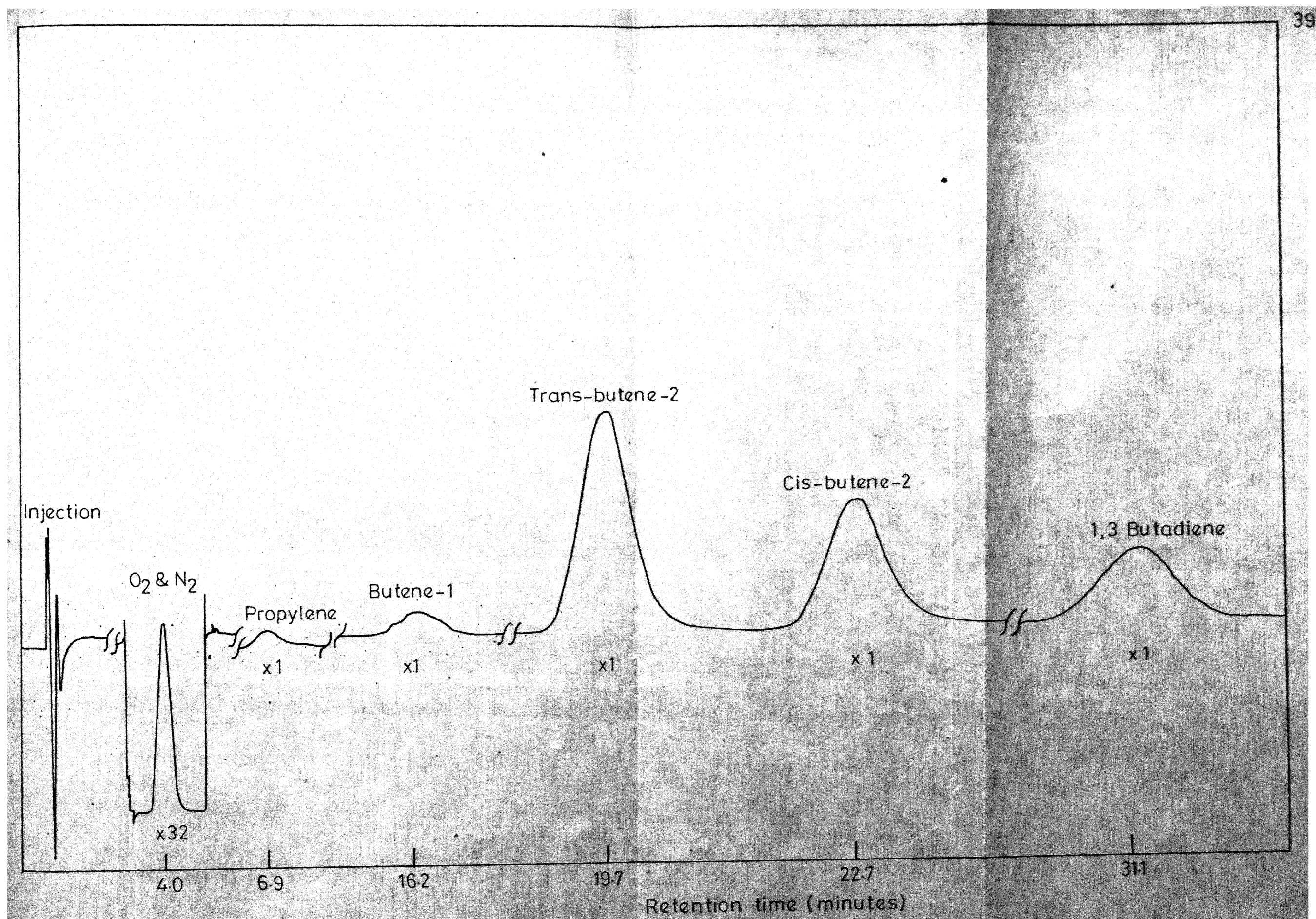
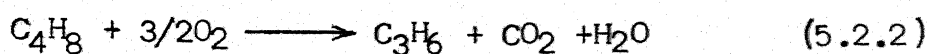
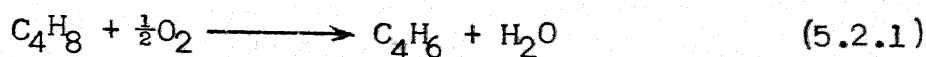


Fig. 8 : Typical chromatogram.

Gas chromatographic analysis of the reactor effluents showed that propylene and butadiene were the main products. Hydrogen and oxygenated organics were totally absent in the product stream. The following reaction take place when butylenes were oxidatively dehydrogenated.



During the preliminary experiments, the exit temperature of reactor was found to be higher by 30-50°C than the temperature at the inlet point of the reactor. This rise in reactor temperature was due to the exothermicity of reactions (5.2.1) and (5.2.2) given above. Because of this large difference in the inlet and outlet reactor temperatures, an average of the two was taken as the effective reactor temperature.

Since carbon dioxide and moisture are highly detrimental for the DMS gas chromatographic column, both carbon dioxide and water were eliminated from the gas samples taken for G.L.C. analysis. The formation of carbon-dioxide during reaction was assumed to be strictly as given by reaction (5.2.2).

The results of various preliminary runs are given in tables 8 to 13.

TABLE - 8

Data for Preliminary Run No. 1

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	10.0
	2. Air	10.0
	3. Steam	21.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	400
	2. Reactor	200
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	3.0
	2. Butene-1	6.2
	3. Trans-Butene-2	61.0
	4. Cis- Butene-2	29.5
	5. 1,3 Butadiene	0.3
IV	<u>Results</u>	
	1. Conversion	3.3%
	2. Yield	0.3%
	3. Selectivity	9.1%
	4. Contact time	1.21 sec.
	5. Butylene:Oxygen:Steam	1:0.2:2.1

TABLE - 9
Data for Preliminary Run No. 2

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	12.0
	2. Air	12.0
	3. Steam	21.0
II	<u>Temperature</u> (°C)	
	1. Preheater	400
	2. Reactor	225
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	3.4
	2. Butene-1	10.8
	3. Trans-Butene-2	53.6
	4. Cis-Butene-2	31.6
	5. 1,3 Butadiene	0.6
IV	<u>Results</u>	
	1. Conversion	4.0%
	2. Yield	0.6%
	3. Selectivity	17.7%
	4. Contact time	1.1 sec.
	5. Butylene: Oxygen: Steam	1:0.2:1.8

TABLE- 10
Data for Preliminary Run No. 3

Sl.No.	Details	Data
I	<u>Flow rates (ml/sec)</u>	
	1. Butylene	8.00
	2. Air	12.00
	3. Steam	20.00
II	<u>Temperatures (°C)</u>	
	1. Preheater	600
	2. Reactor	300
III	<u>Product Composition (vol.%)</u>	
	1. Propylene	94.7
	2. Butene-1	0.
	3. Trans-Butene-2	3.2
	4. Cis-Butene-2	2.1
	5. 1,3 Butadiene	0.
IV	<u>Results</u>	
	1. Conversion	94.7%
	2. Yield	0. %
	3. Selectivity	0. %
	4. Contact time	1.24 sec.
	5. Butylene:Oxygen:Steam	1:0.3:2.5

TABLE- 11

Data for Preliminary Run No. 4

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	18.0
	2. Air	2.0
	3. Steam	21.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	250
	2. Reactor	390
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	2.9
	2. Butene-1	15.8
	3. Trans-Butene-2	46.4
	4. Cis-Butene-2	33.5
	5. 1,3 Butadiene	1.4
IV	<u>Results</u>	
	1. Conversion	4.3%
	2. Yield	1.4%
	3. Selectivity	31.8%
	4. Contact time	1.21 sec.
	5. Butylene: Oxygen : Steam	1:0.02: 1.2

TABLE- 12

Data for Preliminary Run No. 5

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	7.5
	2. Air	33.5
	3. Steam	20.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	250
	2. Reactor	750
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	80.0
	2. Butene-1	12.7
	3. Trans-Butene-2	2.9
	4. Cis-Butene-2	2.4
	5. 1,3 Butadiene	2.0
IV	<u>Results</u>	
	1. Conversion	82.0%
	2. Yield	2.0%
	3. Selectivity	2.5%
	4. Contact time	0.82 sec.
	5. Butylene: Oxygen : Steam	1:1:2.7

TABLE- 13

Data for Preliminary Run No. 6

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	11.5
	2. Air	11.5
	3. Steam	20.5
II	<u>Temperatures</u> (°C)	
	1. Preheater	240
	2. Reactor	900
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	97.0
	2. Butene-1	0.
	3. Trans-Butene-2	2.0
	4. Cis-Butene-2	1.0
	5. 1,3 Butadiene	0.
IV	<u>Results</u>	
	1. Conversion	97.0%
	2. Yield	0. %
	3. Selectivity	0. %
	4. Contact time	1.14 sec.
	5. Butylene:Oxygen:Steam	1:0.2:1.8

5.2.1 Effect of Preheater Temperature :

The preheater temperature was varied in the range of 240 to 600°C . The effect of preheater temperature on conversion, yield and selectivity is shown in table 14.

TABLE- 14
Effect of Preheater Temperature

Sl. No.	Preheater temp. °C	Reactor temp. °C	Results		
			Conver- sion %	Yield %	Selecti- vity %
1	240	240	5.1	3.7	72.5
2	400	225	4.0	0.6	17.7
3	600	300	94.7	0.	0.

It may be noted that the yield and selectivity of butadiene decreased as the preheater temperature was increased. At the temperature of 600°C or above, although the conversion was found to ^{be} very high as 95% but the yield and selectivity were almost zero. This probably happened due to the cracking of butylenes in the preheater. Hence lower temperatures of the preheater should be used. The preheater was maintained in the range of 240-275°C in subsequent runs.

5.2.2 Effect of Oxygen to Butylene Ratio :

To study the effect of oxygen to butylene ratio on conversion, yield and selectivity, the ratios were varied from 0.02 :1 to 0.8:1 . The results are shown in table 15. The preheater temperature^{was} between 240 - 275°C

TABLE - 15

Effect of Butylenes to Oxygen ratio

Sl. No.	Oxygen : Butylene	Reactor Temp. °C	Results		
			Conversion %	Yield %	Selectivity %
1	0.02: 1	390	4.3	1.4	31.8
2	0.8 : 1	380	17.7	15.3	86.4
3	0.5: 1	400	22.1	20.9	95.5

A comparison of run nos .1 and 3, when the reactor temperature was of the same order, 400°C, and the oxygen to butylene ratio was increased by 25 fold, the conversion was found to increase by about five fold and the butadiene selectivity was as high as 95% . This is expected because according to the oxidative dehydrogenation reaction one mole of butylenes requires 0.5 mole of oxygen for complete conversion . Thus a ratio of 0.5 or more should be used for experimental runs .

5.3 Experimental Test Runs :

Based on the exploratory information obtained from the preliminary test runs the detailed experiments were

by
carried out, varying the reactor temperature in the range of
240 to 500°C. The preheater temperature was varied from
240 to 275°C. The detailed experimental data are given in
tables 16 to 23 .

TABLE - 16

Data for Test Run No. 1

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	4.0
	2. Air	8.6
	3. Steam	21.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	240
	2. Reactor	240
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	1.4
	2. Butene-1	2.6
	3. Trans-Butene-2	50.3
	4. Cis-Butene-2	42.0
	5. 1,3 Butadiene	3.7
IV	<u>Results</u>	
	1. Conversion	5.1%
	2. Yield	3.7%
	3. Selectivity	72.5%
	4. Contact time	1.5 sec.
	5. Butylene:Oxygen:Steam	1:0.45:5.2

TABLE - 17

Data for Test Run No. 2

Sl. No.	Details	Data
I	<u>Flow rates</u> (ml/sec.)	
	1. Butylene	7.6
	2. Air	12.0
	3. Steam	21.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	240
	2. Reactor	275
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	1.3
	2. Butene-1	5.4
	3. Trans-Butene-2	50.7
	4. Cis-Butene-2	37.3
	5. 1,3 Butadiene	5.3
IV	<u>Results</u>	
	1. Conversion	6.6 %
	2. Yield	5.3 %
	3. Selectivity	80.4 %
	4. Contact time	1.22 sec.
	5. Butylene: Oxygen : Steam	1:0.33: 2.8

TABLE - 19

Data for Test Run No. 4

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec)	
	1. Butylene	8.0
	2. Air	30.0
	3. Steam	20.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	275
	2. Reactor	360
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	0.8
	2. Butene-1	1.8
	3. Trans-Butene-2	56.1
	4. Cis-Butene -2	31.1
	5. 1, 3 Butadiene	10.2
IV	<u>Results</u>	
	1. Conversion	11.0%
	2. Yield	10.2%
	3. Selectivity	92.7%
	4. Contact time	0.86 sec.
	5. Butylene :Oxygen :Steam	1:0.80: 2.5

TABLE - 20
Data for Test Run No. 5

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec.)	
	1. Butylene	8.7
	2. Air	32.7
	3. Steam	20.0
II	<u>Temperatures</u> (°C)	
	1. Preheater	240
	2. Reactor	380
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	2.4
	2. Butene-1	18.6
	3. Trans-butene-2	39.3
	4. Cis-Butene-2	24.4
	5. 1, 3 Butadiene	15.3
IV	<u>Results</u>	
	1. Conversion	17.7%
	2. Yield	15.3%
	3. Selectivity	86.4%
	4. Contact time	0.81 sec.
	5. Butylene:Oxygen:Steam	1:0.81: 2.7

TABLE - 21
DATA FOR TEST RUN NO. 6

Sl. No.	Details	Data
I	<u>Flow rates</u> (ml/sec.)	
	1. Butylene	6.0
	2. Air	15.0
	3. Steam	20.5
II	<u>Temperatures</u> (°C)	
	1. Preheater	240
	2. Reactor	380
III	<u>Product Composition</u> (vol.%)	
	1. Propylene	2.1
	2. Butene- 1	17.2
	3. Trans- Butene-2	41.1
	4. Cis- Butene-2	24.6
	5. 1, 3 Butadiene	15.0
IV	<u>Results</u>	
	1. Conversion	17.1%
	2. Yield	15.0%
	3. Selectivity	88.2%
	4. Contact time	1.21 sec.
	5. Butylene: Oxygen: Steam	1:0.53:3.3

TABLE- 22

Data for Test Run No. 7

Sl.No.	Details	Data
I	<u>Flow rates</u> (ml/sec.)	
	1. Butylene	6.0
	2. Air	15.0
	3. Steam	20.5
II	<u>Temperatures</u> (C)	
	1. Preheater	275
	2. Reactor	400
III	<u>Product Compositions</u> (vol.%)	
	1. Propylene	1.2
	2. Butene-1	3.2
	3. Trans-Butene-2	46.2
	4. Cis-Butene-2	28.5
	5. 1, 3 Butadiene	20.9
IV	<u>Results</u>	
	1. Conversion	22.1%
	2. Yield	20.9%
	3. Selectivity	94.5%
	4. Contact time	1.21 sec.
	5. Butylene:Oxygen:Steam	1:0:0.53:3.3

The data for the effect of reactor temperature on conversion, yield and selectivity (including a few preliminary test runs) in the range of 240 to 900°C are shown in table 24.

TABLE - 24

Effect of Reactor Temperature on Conversion, Yield and Selectivity

Sl. No.	Reactor Temperature °C	Data		
		Conversion %	Yield %	Selectivity %
1	240	5.1	3.7	72.5
2	275	6.6	5.3	80.4
3	340	8.6	5.8	67.5
4	360	11.0	10.2	92.7
5	380	17.7	15.3	86.4
6	400	22.1	20.9	94.5
7	500	26.2	24.6	94.0
8	750	82.0	2.0	2.5
9	900	97.0	0.	0.

A reference to run nos. 8 and 9 in the above table would indicate that at temperatures above 750°C although conversion increased, the yield and the selectivity with

respect to butadiene decreased very rapidly and at 900°C they dropped to zero. This probably may be due to the predominant cracking reactions at higher temperatures of 750 to 900°C .

It may also be noted that at lower reactor temperatures about (240°C), the conversion of butylenes was very low at about 5% with butadiene selectivity of about 72%.

5.3.1 . Effect of Temperature on Conversion :

Figure 9 shows the effect of temperature on conversion. It may be noted that the conversion of butylenes increased **almost** linearly with temperature.

5.3.2 Effect of Temperature on Yield :

Figure 10 shows the effect of reactor temperature on yield. The yield of butadiene also increased almost linearly with temperature .

5.3.3 Effect of Temperature on Selectivity :

Figure 11 shows the effect of reactor temperature on the selectivity with respect to butadiene. The selectivity increased with temperature upto 350°C and then remained almost constant over the temperature range 400 to 500°C , which may be considered as the optimum temperature range.

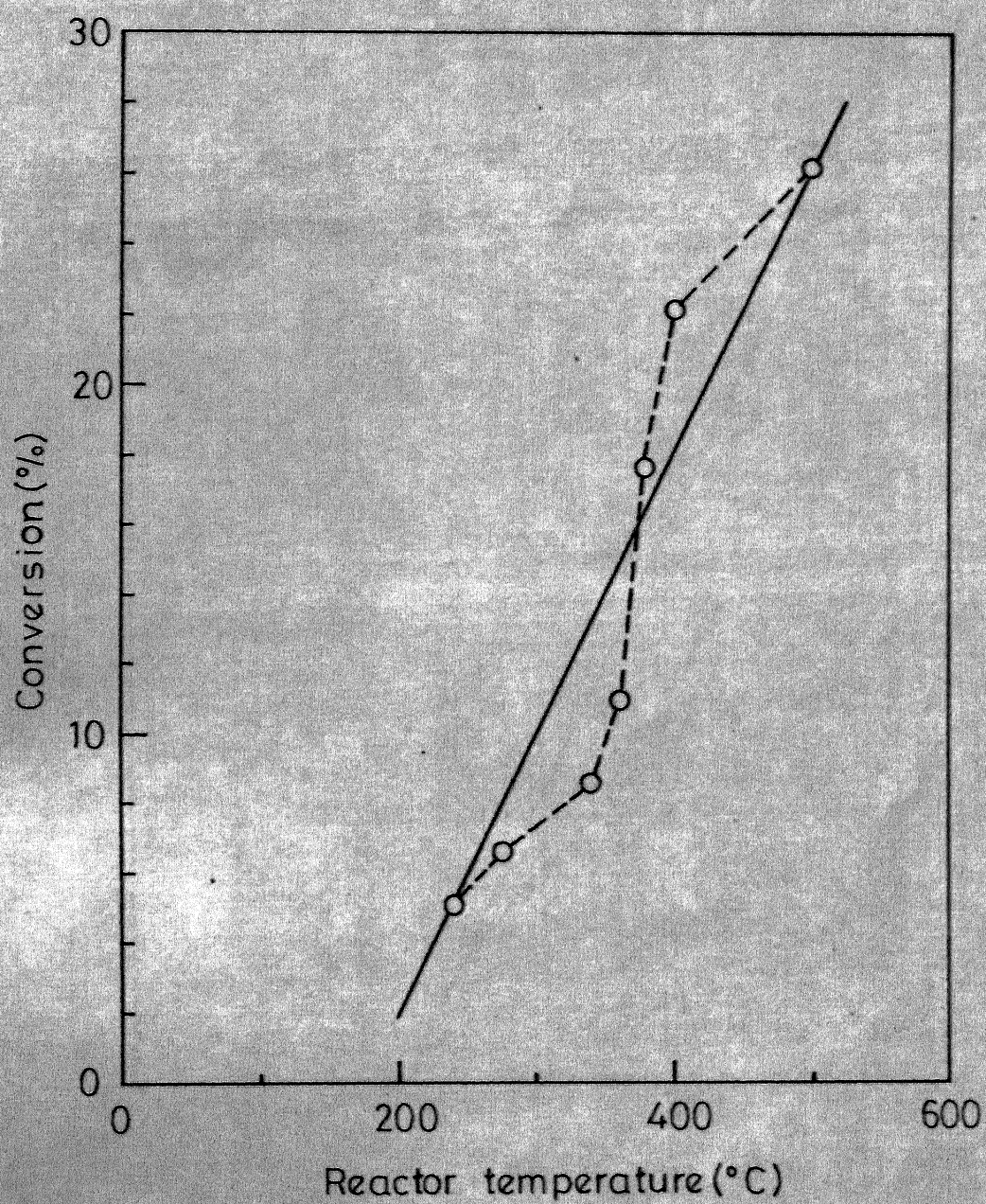


Fig. 9 : Effect of reactor temperature on conversion.

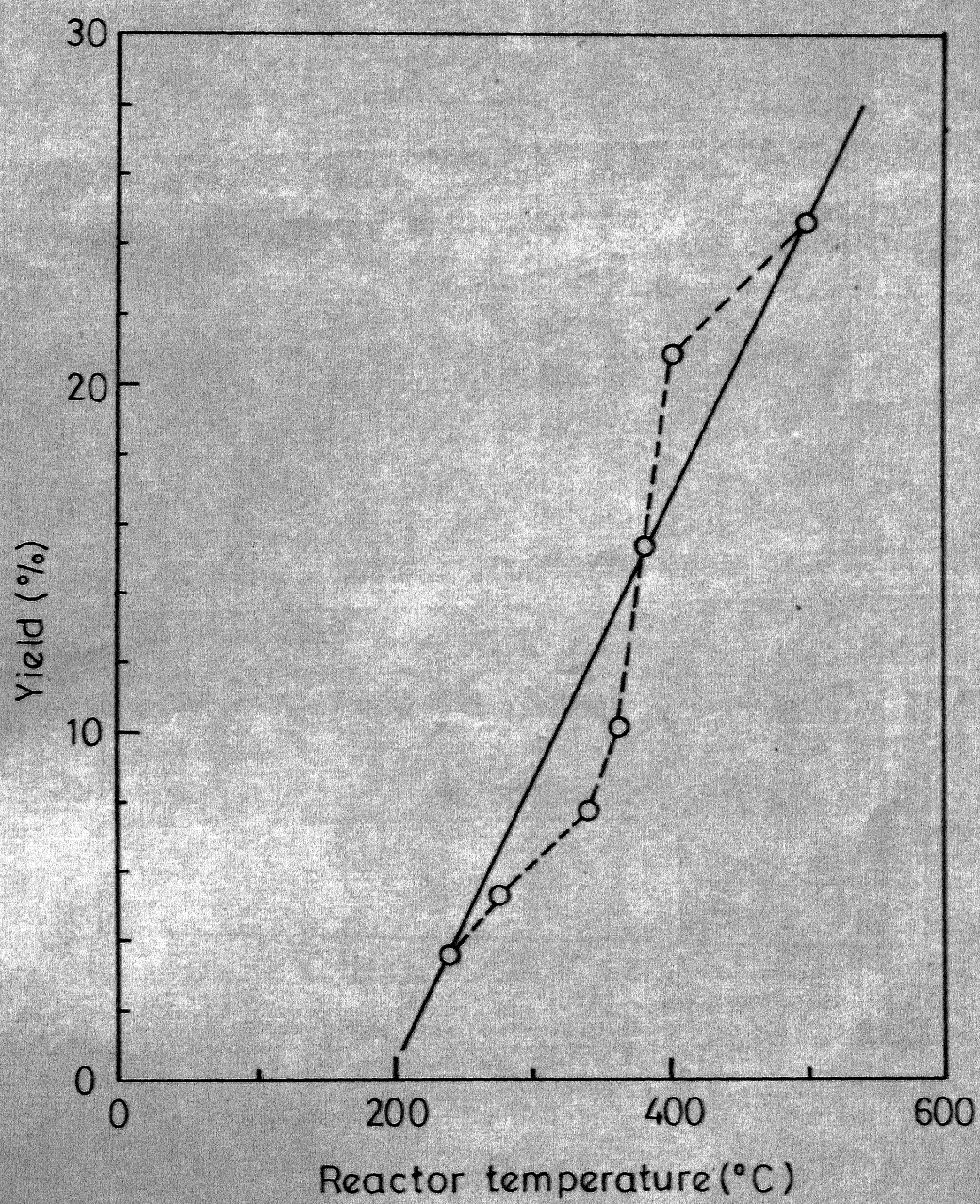


Fig. 10 : Effect of reactor temperature on yield.

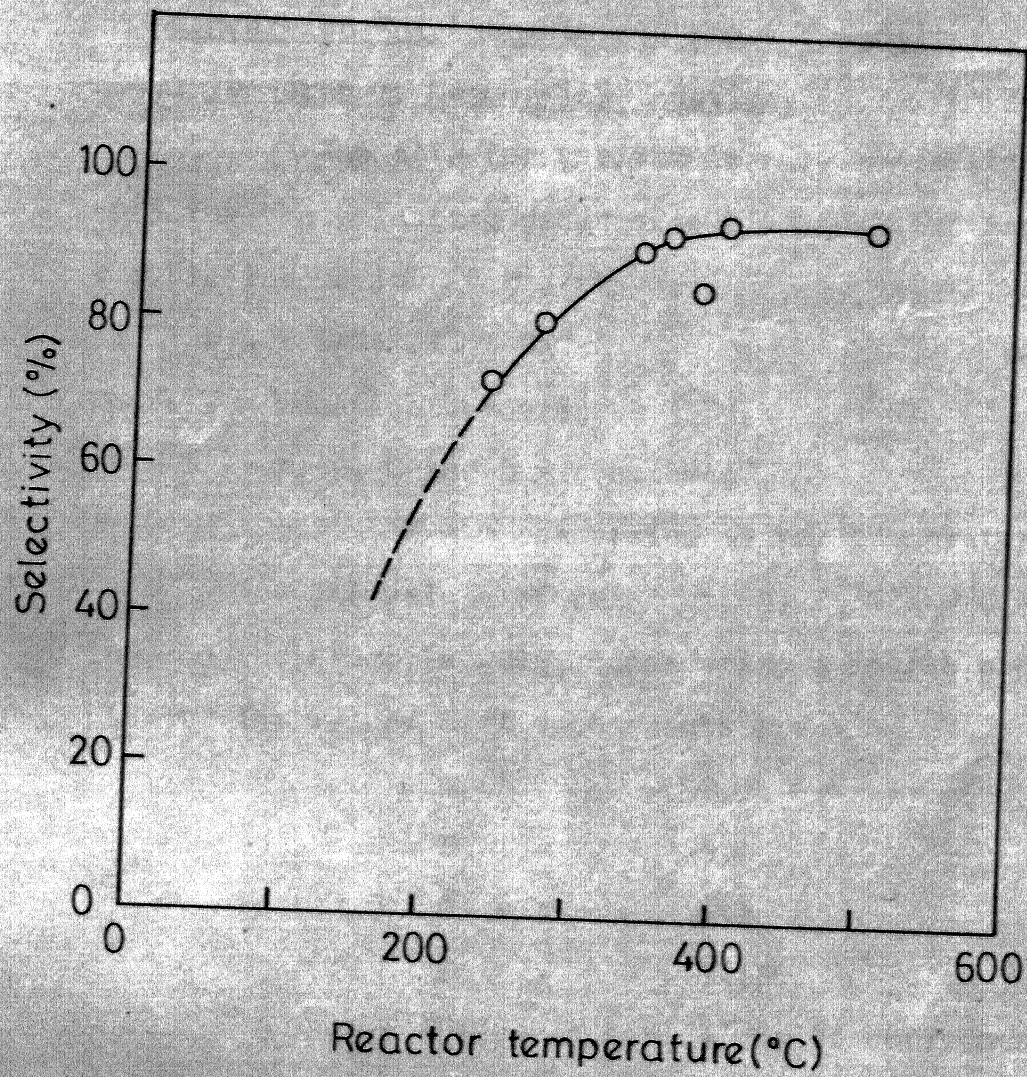


Fig. 11 : Effect of reactor temperature on selectivity.

5.4 Development of Empirical Equations for Temperature

Conversion Relationship and Kinetic Model :

5.4.1 Temperature Conversion Equation :

The data for the temperature conversion relationship for the oxidative dehydrogenation reaction may be given by a cubical equation of the type :

$$T = A + BX + CX^2 + DX^3 \quad (5.4.1)$$

Where T = reaction temperature ($^{\circ}\text{C}$)

A, B, C and D = constants

X = % conversion at any temperature T.

The values of constants A, B, C and D were determined by the Cramer's rule, considering a fourth order determinant. The values of the constants are :

$$\begin{array}{rcl} A & = & - 99.0 \\ B & = & 95.0 \\ C & = & - 6.3 \\ D & = & 0.136 \end{array}$$

Substitution of the values of constants in equation (5.4.1) gives :

$$T = - 99.0 + 95.0 X - 6.3 X^2 + 0.136 X^3 \quad (5.4.2)$$

Equation 5.4.2 correlates the temperature-conversion data obtained for the oxidative dehydrogenation reaction over the temperature range of $240\text{--}500^{\circ}\text{C}$ with a deviation of $\pm 2.0\%$. However the equation can not be used to extrapolate values outside the given temperature range.

5.4.2 Kinetics of Reaction :

Serebrayakov³⁸ and his coworkers reported that oxidative dehydrogenation follows the first order kinetics. Bakshi³⁹ also found that reaction is first order (0.5 order in butylenes and 0.5 order in oxygen). Accordingly, the data obtained in this study for the rate of conversion of butylenes may be described by an over all first order kinetics, that is,

$$r_A = K C_A^{0.5} C_B^{0.5} \quad \dots \quad (5.4.3)$$

Where

$$\begin{aligned} r_A &= \text{rate of conversion of butylenes} \\ &= \frac{\text{g-mole of butylenes converted}}{(\text{sec.}) (\text{cm}^3 \text{ of catalyst})} \\ K &= \text{rate constant (sec.}^{-1}\text{)} \\ C_A &= \text{Concentration of butylenes (g-mole/cm}^3\text{)} \\ C_B &= \text{Concentration of oxygen (g-mole/cm}^3\text{)} \end{aligned}$$

If

$$\begin{aligned} C_{A0} &= \text{Initial concentration of butylenes (g-mole/cm}^3\text{)} \\ C_{B0} &= \text{Initial concentration of oxygen (g-mole/cm}^3\text{)} \\ X_A &= \text{Conversion of butylenes} \\ \epsilon_A &= \text{Fractional volume change on complete conversion of butylenes.} \end{aligned}$$

Then a more generalized form of equation (5.4.3) may be written as⁴⁰ :

$$r_A = \frac{K C_{AO} (1 - X_A)^{0.5} (M - X_A/2)^{0.5}}{(1 + G_A X_A)} \quad (5.4.4)$$

Where

$$M = C_{BO}/C_{AO}$$

Now, $G_A = 1/3$ (For the equation (5.2.1))

$$\text{which gives } r_A = \frac{3 K C_{AO} (1 - X_A)^{0.5} (M - X_A/2)^{0.5}}{(3 + X_A)} \quad (5.4.5)$$

5.4.3 Reaction Rate Constant :

The values of reaction rate constant in the temperature range of 340- 500°C were determined by using the expression (5.4.5) . The data are given in table 25.

TABLE - 25

Reaction Rate Constant

Sl.No.	Temperature(°C)	K(sec. ⁻¹)
1	340	0.53
2	360	0.56
3	380	1.00
4	400	1.17
5	500	1.80

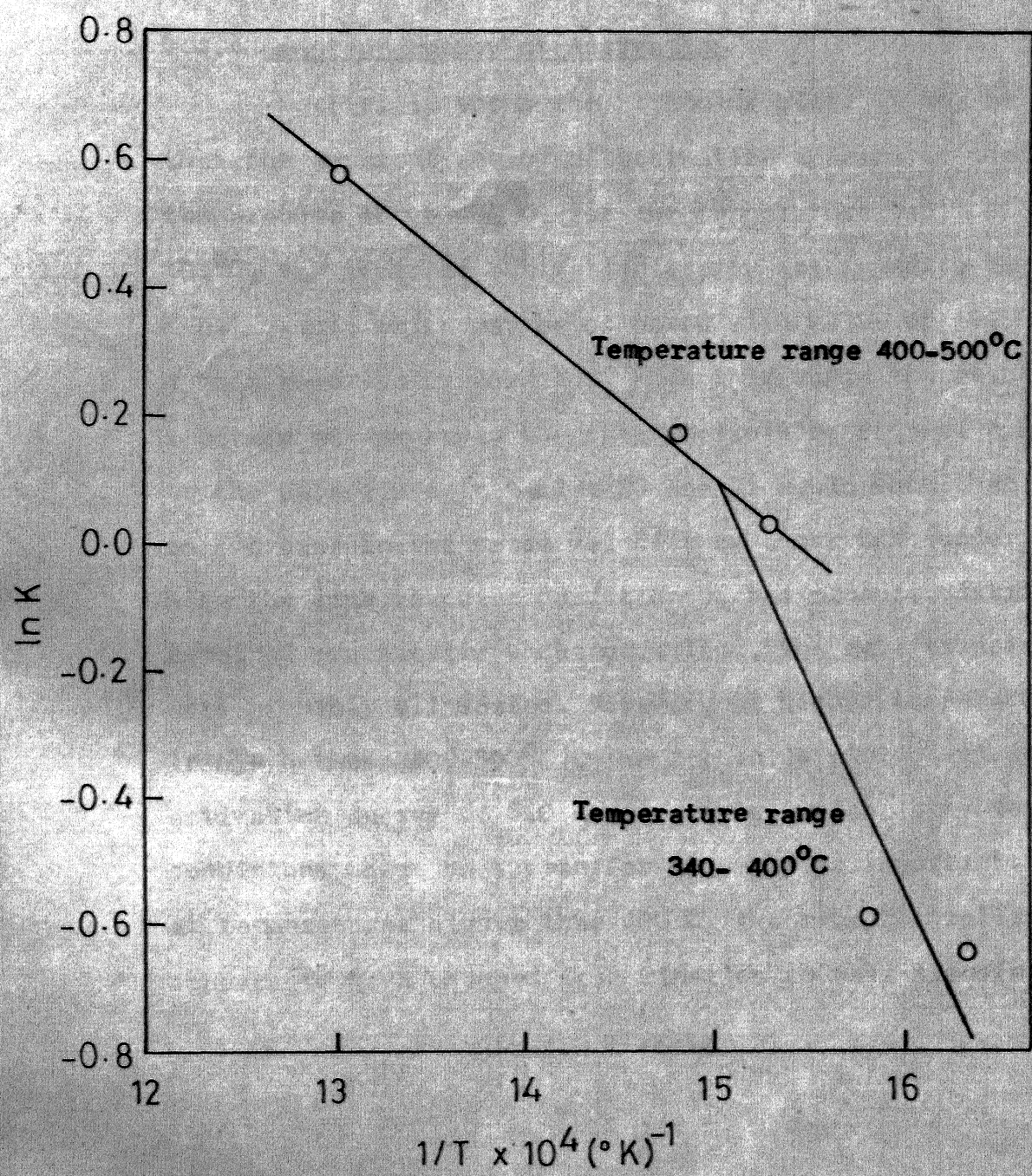


Fig. 12 : Arrhenius plot.

5.4.4 Apparent Energy of Activation :

Fig. 12 shows the Arrhenius plot. It may be noted that the apparent energy of activation appears to change at temperature above 400°C . For the temperature range of $340-400^{\circ}\text{C}$, the apparent activation energy was found to be $13.0 \text{ K-cal/g-mole}$ which may be compared with value of $14.5 \text{ K-cal/g mole}$ reported by Boreskov.⁴¹ In this range the reaction kinetics was probably the rate controlling regime. A reference to the data given in tables 20 and 21 would show that at 380°C , an increase in the space velocity by about 50% (under otherwise the same reaction conditions), the product distributions remained practically unchanged. Thus, the mass transfer factors were probably eliminated. However, at higher temperatures, (range between $400-500^{\circ}\text{C}$), the Arrhenius plot gives an apparent activation energy of 6.0 K-cal/g.mole , which is typical of conditions where mass transfer step may be important. Hence, at temperatures higher than 400°C , the rate controlling regime appears to have changed from kinetics to mass transfer .

CHAPTER - VI

CONCLUSIONS

CHAPTER - VI

CONCLUSIONS

The oxidative dehydrogenation of butylenes to butadiene using a catalyst consisting of Fe_2O_3 , MgO and Cr_2O_3 on Al_2O_3 as the carrier was studied over the temperature range of 200-900°C. The oxygen to butylenes ratio was varied from 0.02 to 0.8 and the steam to butylenes ratio was varied from 1.8 to 5.2. The butylene preheater temperature was varied from 200-600°C.

The best results were obtained for the reactor temperature range of 340-500°C, preheater temperature in the range of 240-275°C and with oxygen to butylene ratio of more than 0.5. The per pass maximum yield of butadiene was found to be 24.6% at 500°C with a butylene conversion of 26.2% and the selectivity with respect to butadiene of 94.0%. The data were correlated by a first order kinetics model. The values of the reaction rate constant at 340 and 500°C were 0.53 and 1.80 sec^{-1} respectively. The apparent activation energy was found to be 13.0 K cal/g-mole in the temperature range of 340-400°C and 6.0 K-cal/g-mole in the range of 400-500°C.

The information obtained during this study is likely to be found useful for an economic utilization of the by-product butylene stream from an ethanol based butadiene plant for conversion to butadiene.

CHAPTER - VII

SUGGESTIONS- FOR- FURTHER WORK

CHAPTER - VII

SUGGESTIONS-FOR-FURTHER WORK

During the present study the maximum conversion of butylenes was found to be 26.2% with a butadiene selectivity of 94.4% at 500°C. This is very low in comparison with the results obtained by Huston¹⁶ and Others^{17,19}, who have reported conversions of the order of 80% and Selectivity of butadiene of 92% at 500°C.

The catalyst used in this study appears to be reasonably good and the low conversions may be due to the following reasons :

As discussed elsewhere (chapter II) the thermodynamic considerations of the conventional reaction (2.1.1) indicate that the conversion of butylenes to butadiene is favourable at lower hydrocarbon partial pressures, which could be achieved by adding a diluent such as steam. Further during the oxidative dehydrogenation of butylenes to butadiene one mole of butylenes and 0.5 mole of oxygen produce one mole of butadiene and one mole of water on complete conversion. This leads to an increase in the volume of the system. Hence a reduction in the pressure of the system should favour the forward reaction and hence the conversion .

The major aim of using steam as a feed to the reactor during the oxidative dehydrogenation Reaction was to

achieve the above task of obtaining lower partial pressures of butylenes and hence higher conversions. However, in the present study the steam generator proved to be of inadequate capacity. It was not possible to increase the steam to butylene ratio of more than 5.0 as compared to the very high ratios of 30- 50 used by other workers.^{16,17,19,41,42} The hydrocarbon partial pressure under the conditions of this study was of the order of 400 mm Hg which would give conversions of about 30% from the thermodynamic considerations as may be noted from the data given in table-2 (chapter II). Higher ratios of steam to butylene would reduce the effective hydrocarbon partial pressure and favour the forward reaction and hence the butylene conversion .

There was yet another constraint in the present study with respect to the supply of butylenes. The amount of butylenes generated in the laboratory by dehydration of secondary butanol and stored in aspirator bottles was of limited supply. It was not possible to obtain more than about 30 minutes supply of butylenes for any run.

In view of the above constraints, the present work may be considered as a preliminary study of the reaction conditions. It is suggested that further work may be carried out by using bottled butylenes and by using a steam generator of adequate capacity to obtain more meaningful results.

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